

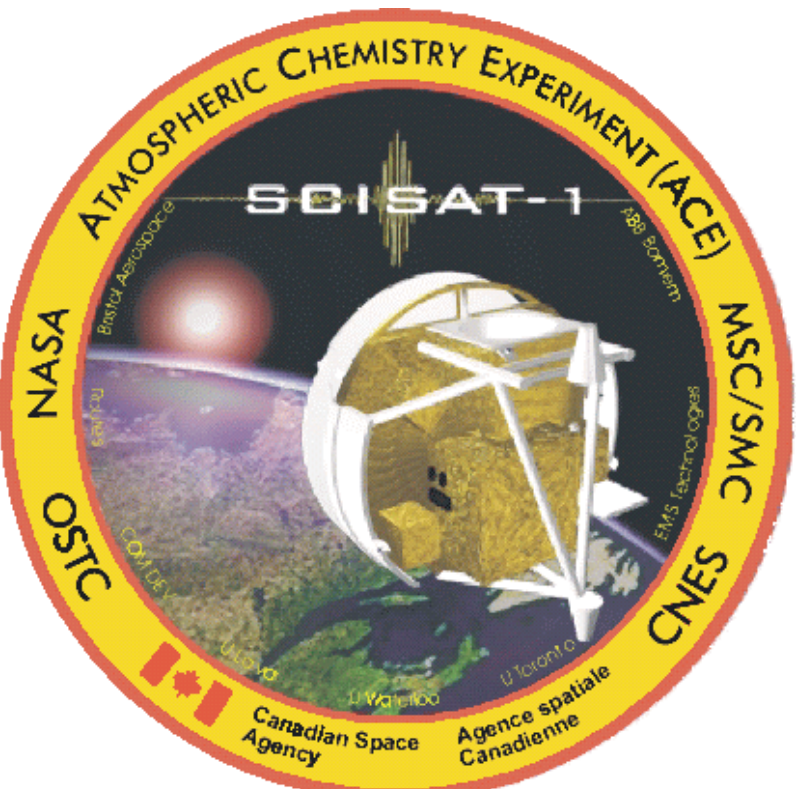
# Global Methyl Chloride Distribution from ACE-FTS Solar Occultation Measurements

Natalie Weigum<sup>1</sup>, Clare McElcheran<sup>1</sup>, Kaley A. Walker<sup>1,2</sup>, Chris Boone<sup>2</sup>, Peter F. Bernath<sup>2,3</sup>, Geoffrey C. Toon<sup>4</sup>, Gloria Manney<sup>4</sup>, Susan Strahan<sup>5</sup>, Bryan Duncan<sup>5</sup>, Yasuko Yoshida<sup>5</sup>, and Yuhang Wang<sup>6</sup>

<sup>1</sup> Department of Physics, University of Toronto, Toronto, Ontario, Canada, <sup>2</sup> Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

<sup>3</sup> Department of Chemistry, University of York, Heslington, York, UK <sup>4</sup> Jet Propulsion Laboratory, Pasadena, CA, USA

<sup>5</sup> Goddard Earth Science and Technology Center, University of Maryland, Baltimore County, USA, <sup>6</sup> School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA USA



## Introduction

One of the most abundant chlorine-containing molecules in the atmosphere is methyl chloride ( $\text{CH}_3\text{Cl}$ ); a species whose sources are almost entirely natural (WMO, 2007). The most common sources of methyl chloride are tropical plants, senescent or dead leaves and biomass burning as well as more minor sources including oceans, salt marshes and industrial emissions. Its main sink is reaction with the hydroxyl radical and its minor sinks are absorption by soil and photolysis in the stratosphere. As the impacts of the Montreal Protocol and its subsequent amendments are becoming apparent in the reduction of chlorofluorocarbons in the atmosphere, naturally-produced methyl chloride is playing an increasingly significant role in the atmospheric ozone budget.

While much is known about the concentration of methyl chloride at the lowest levels of the atmosphere from *in situ* techniques, there are relatively few measurements of its altitude distribution at higher altitudes. In this work, we will focus on the remote sensing studies of methyl chloride in the upper troposphere and the stratosphere. Methyl chloride was first detected in infrared spectroscopic measurements by the Atmospheric Trace MOlecule Spectroscopy (ATMOS) experiment on-board the Space Shuttle during the Spacelab 3 mission [Park *et al.*, 1986]. Profiles of methyl chloride were retrieved from ATMOS data collected on a total of four Shuttle flights and were used in calculations of the stratospheric chlorine inventory at mid- and subtropical latitudes [Zander *et al.*, 1992; Zander *et al.*, 1996]. The MkIV balloon-borne Fourier transform spectrometer (FTS) has made measurements of methyl chloride since 1997 [Toon *et al.*, 1999]. This instrument makes approximately one flight per year from different sites around the world including Fort Sumner, NM, Kiruna, Sweden and, Fairbanks, Alaska. Because of the relatively short durations of their flights, both the ATMOS and MkIV measurements are limited in their spatial and temporal coverage. To date, there is no global picture of the distribution of methyl chloride obtained from observations.

This poster presents the first study of the global distribution of methyl chloride in the stratosphere and upper troposphere using measurements from the infrared FTS on board the Atmospheric Chemistry Experiment (ACE) satellite. These results are compared with those from the MkIV interferometer and from two chemical transport models. Output from the Global Modeling Initiative (GMI) Combined Stratospheric-Tropospheric Model driven by assimilated meteorological fields [Strahan *et al.*, 2007; Duncan *et al.*, 2007] was used as well as results obtained from inverse modeling of the sources of methyl chloride using the GEOS-Chem model [Yoshida *et al.*, 2006].

## ACE-FTS Profiles

The primary instrument on-board ACE is a high-resolution ( $0.02\text{ cm}^{-1}$ ) Fourier Transform Spectrometer (FTS) operating between  $750$  and  $4400\text{ cm}^{-1}$  [Bernath *et al.*, 2005]. The satellite was launched on 12 August 2003 and has been operating routinely since late February 2004. ACE-FTS uses the solar occultation technique (Figure 1) to obtain measurements of the Earth's atmosphere from the upper troposphere to the lower thermosphere. The transmittance spectra from the sunrise and sunset measurements are used to determine atmospheric profiles of over 30 trace gases, temperature, pressure and atmospheric extinction.

Methyl chloride is retrieved from ACE-FTS occultation spectra between 9 and 40 km, using three microwindows between  $2965$  and  $2968\text{ cm}^{-1}$  and one at  $1460\text{ cm}^{-1}$  [Boone *et al.*, 2005]. The main interfering species are ozone, methane, water vapour and ethane. The profiles used here are a research product that improves on the version 2.2 retrievals by including pseudo-lines to account for ethane absorptions that are not reported in the HITRAN database. Without including these ethane lines in the retrieval, the methyl chloride volume mixing ratios (VMRs) at the lowest altitudes are overestimated by up to 100 pptv.

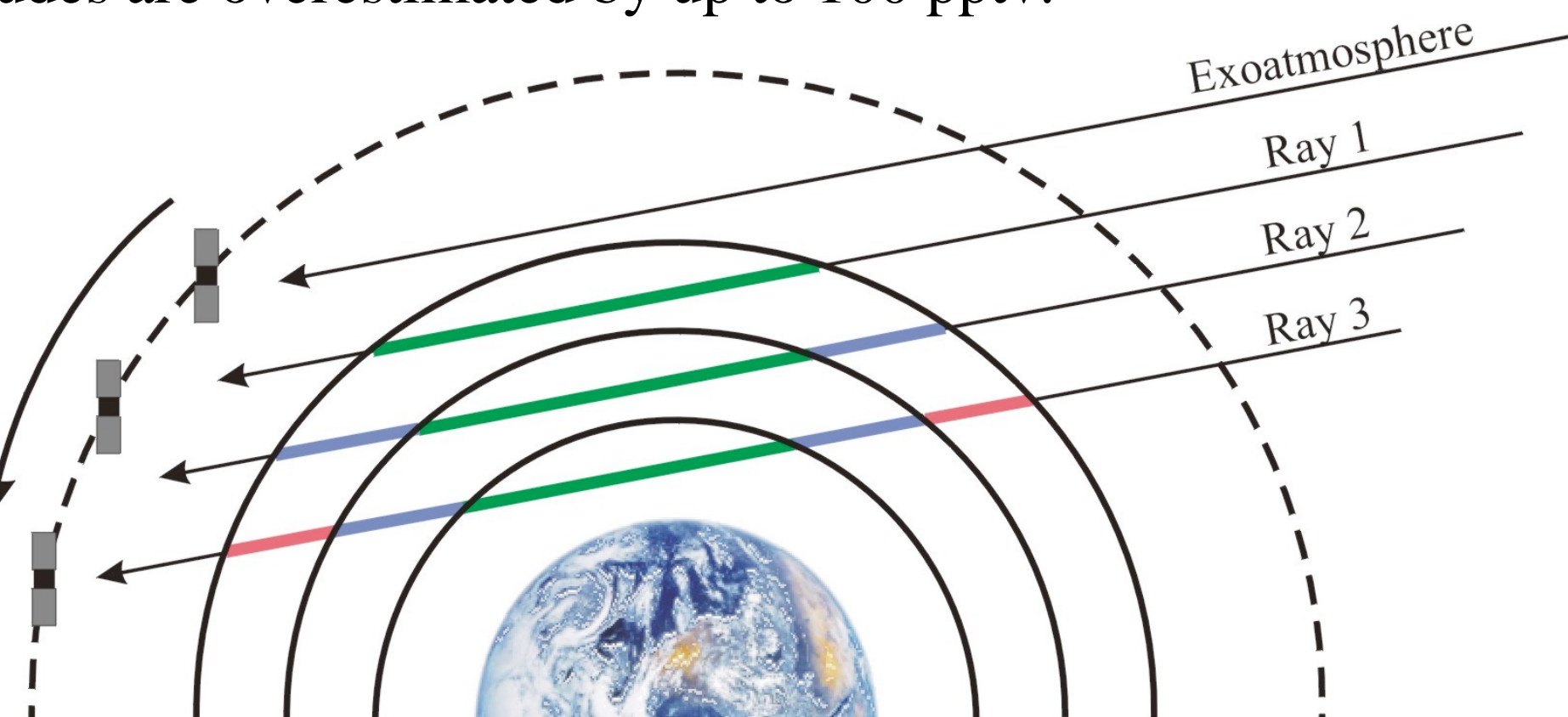


Figure 1. Schematic diagram showing the occultation measurement sequence for a sunset observation.

## $\text{CH}_3\text{Cl}$ Zonal Mean Profiles from ACE-FTS

In our first analysis, the ACE-FTS occultations from 21 February 2004 to 30 March 2007 were separated into six broad latitude bands and averaged to produce zonal mean profiles of methyl chloride. Those profiles located on the edge or within the polar vortex were excluded, so a total of 11,027 occultations were included in the analyses. The zonal mean profiles for each of the  $30^\circ$  latitude bands are shown in Figure 2. When these calculations were repeated with data divided by year (2004, 2005, and 2006), the differences between years were found to be smaller than the standard deviations of the means. Therefore all calculations have been done using the entire three-year dataset. The highest methyl chloride VMRs were found in the tropics and subtropics and these concentrations decrease towards the poles. This is consistent with the major sources being tropical plants, biomass burning and decomposing leaves.

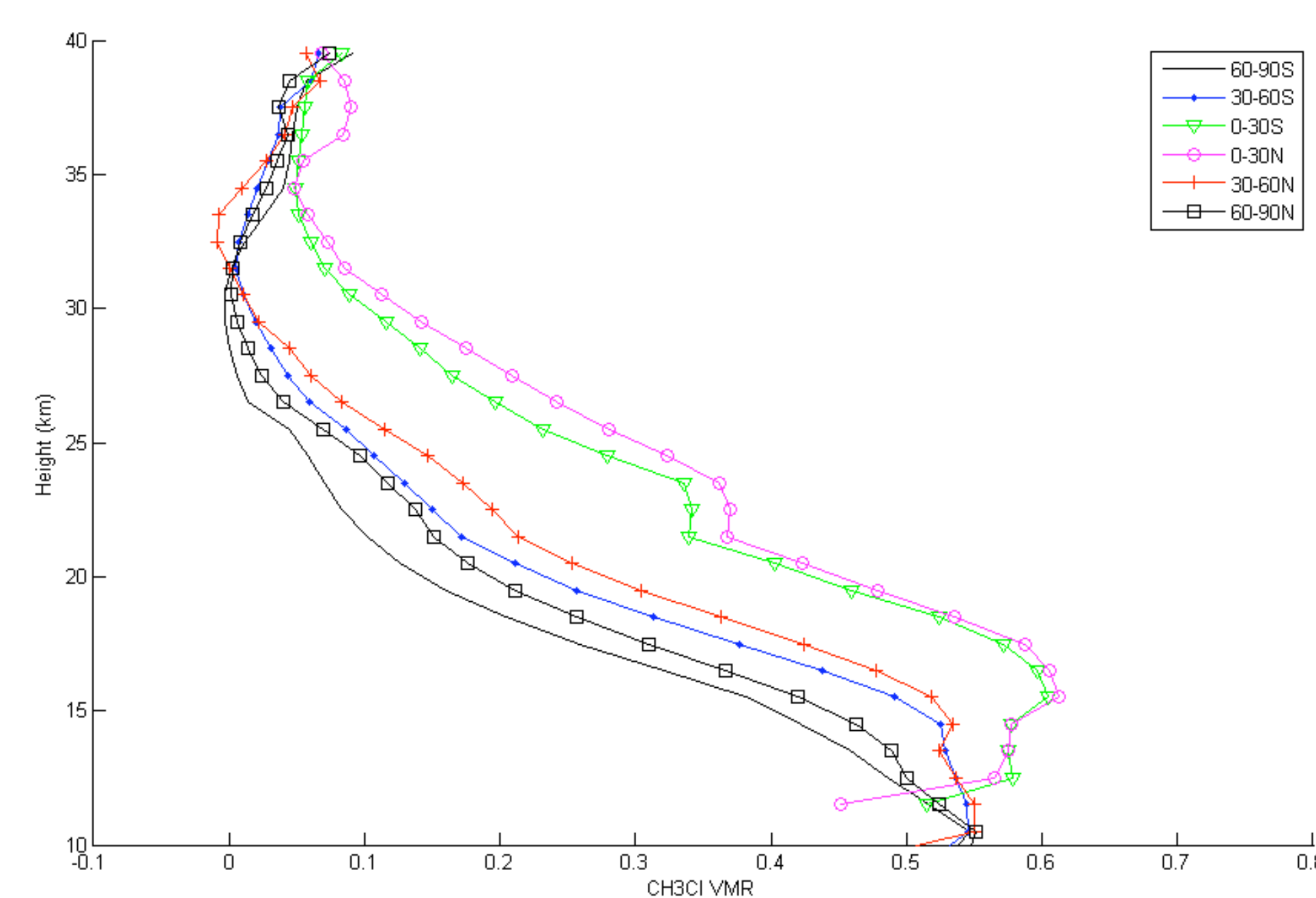
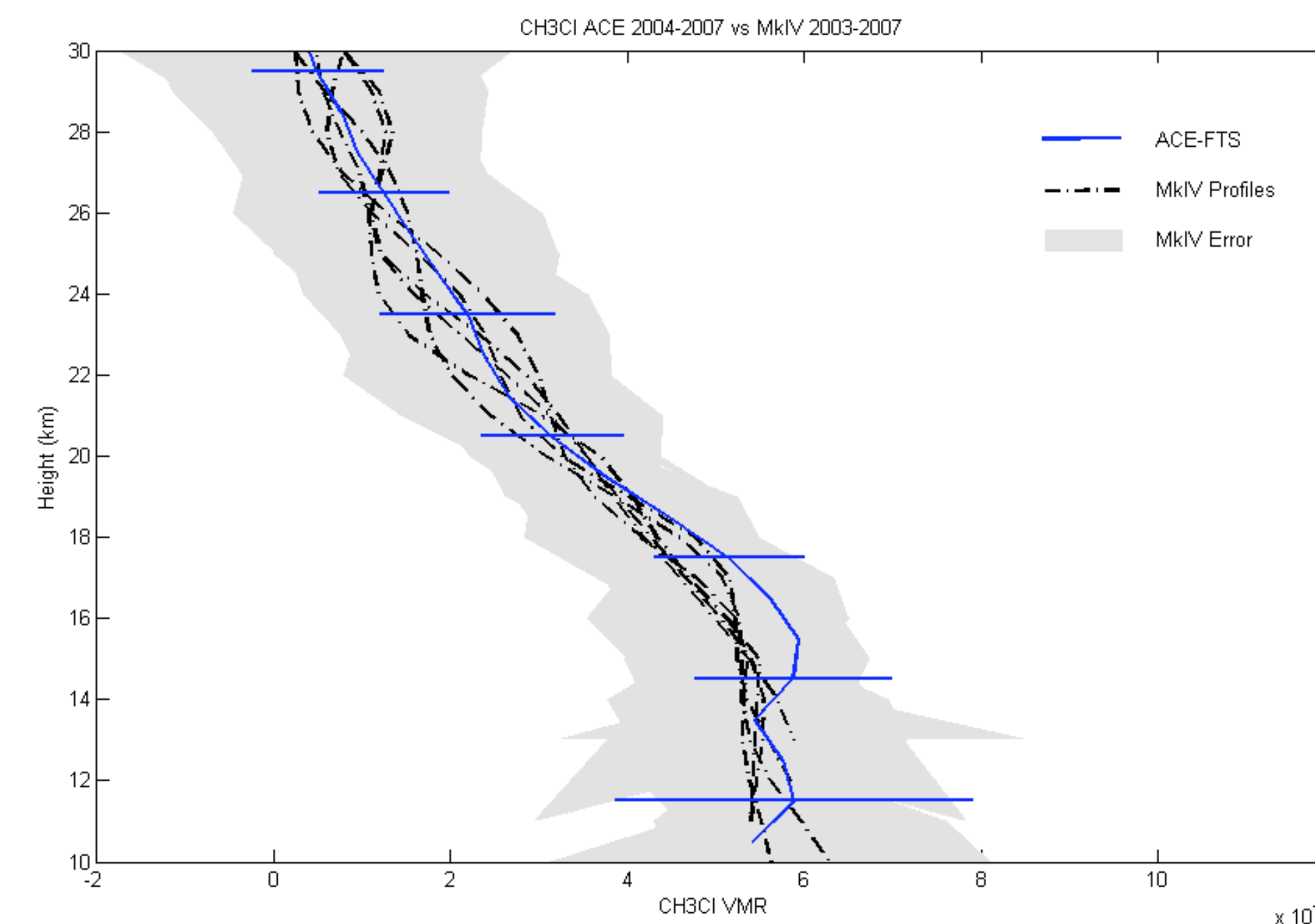


Figure 2. Zonal mean profiles of methyl chloride VMRs in ppbv. The plot shows the six latitude bands covering northern (NH) and southern (SH) hemisphere tropics and subtropics, mid-latitudes and polar regions. Data from all years (2004-2007) were included. The differences between the NH and SH for each latitude band are smaller than the standard deviations of the means (not shown but of similar magnitude to those shown in Figure 3).

## Comparison of ACE-FTS and MkIV profiles

MkIV is an infrared FTS designed to measure profiles of atmospheric species from a high-altitude balloon platform using the solar absorption spectrometry [Toon *et al.*, 1999]. Recent MkIV campaign results from Ft. Sumner, NM ( $35^\circ\text{N}$ ,  $110^\circ\text{W}$ ) in Fall 2003, 2004, 2005, and 2007 were compared with a zonal average of the 2004 - 2007 ACE-FTS measurements from August - October over the latitudes  $25$  to  $45^\circ\text{N}$  (Figure 3). The measurements agree well within the uncertainty of the MkIV data. Between 11 and 30 km, the percent differences range from 0.1% to less than 10%.

Figure 3. Comparison of zonal mean profiles of methyl chloride VMRs (in ppbv) from the MkIV balloon observations near Ft. Sumner, NM and from the ACE-FTS. The balloon-borne measurements took place during fall turnaround. Error bars on ACE-FTS data are standard deviation of the mean. The shaded areas are the 1-sigma errors from the MkIV retrievals.



## Comparison of ACE-FTS Zonal Mean Profiles with Models

To compare with the model results, the set of ACE-FTS extravortex profiles from 21 February 2004 to 30 March 2007 have been averaged within  $5^\circ$  bins in latitude and 3 km bins in altitude to produce zonal mean profiles. The altitude bin size was chosen to match the 3-4 km vertical resolution of the ACE-FTS measurements. The model results from the GMI combo model and the GEOS-Chem inversion have been averaged using the same latitude and altitude bin sizes. The Aura period 4 run (February 2004 - December 2006) of the GMI combo model was used for the comparison. The meteorological fields were taken from the GEOS-4 Data Assimilation System [Bloom *et al.*, 2005] and the model spatial resolution was  $2^\circ$  latitude x  $2.5^\circ$  longitude with 42 levels (model lid at 0.01 hPa). The inverse modeling of global methyl chloride results from Yoshida *et al.* [2006] used the GEOS-Chem global 3-D chemical transport model (v. 5.02) as the forward model [Bey *et al.*, 2001]. The horizontal resolution was  $4^\circ$  latitude x  $5^\circ$  longitude and 26 vertical levels were used. The time period for the meteorological fields used was August 1996 to September 1997, corresponding to times of the aircraft and ground-based measurements used in the inversion. Monthly results from the GMI Aura4 run were used in the averages for the comparisons with ACE-FTS, as only a relatively small difference was found when sampling the daily model data to match the locations of the ACE observations.

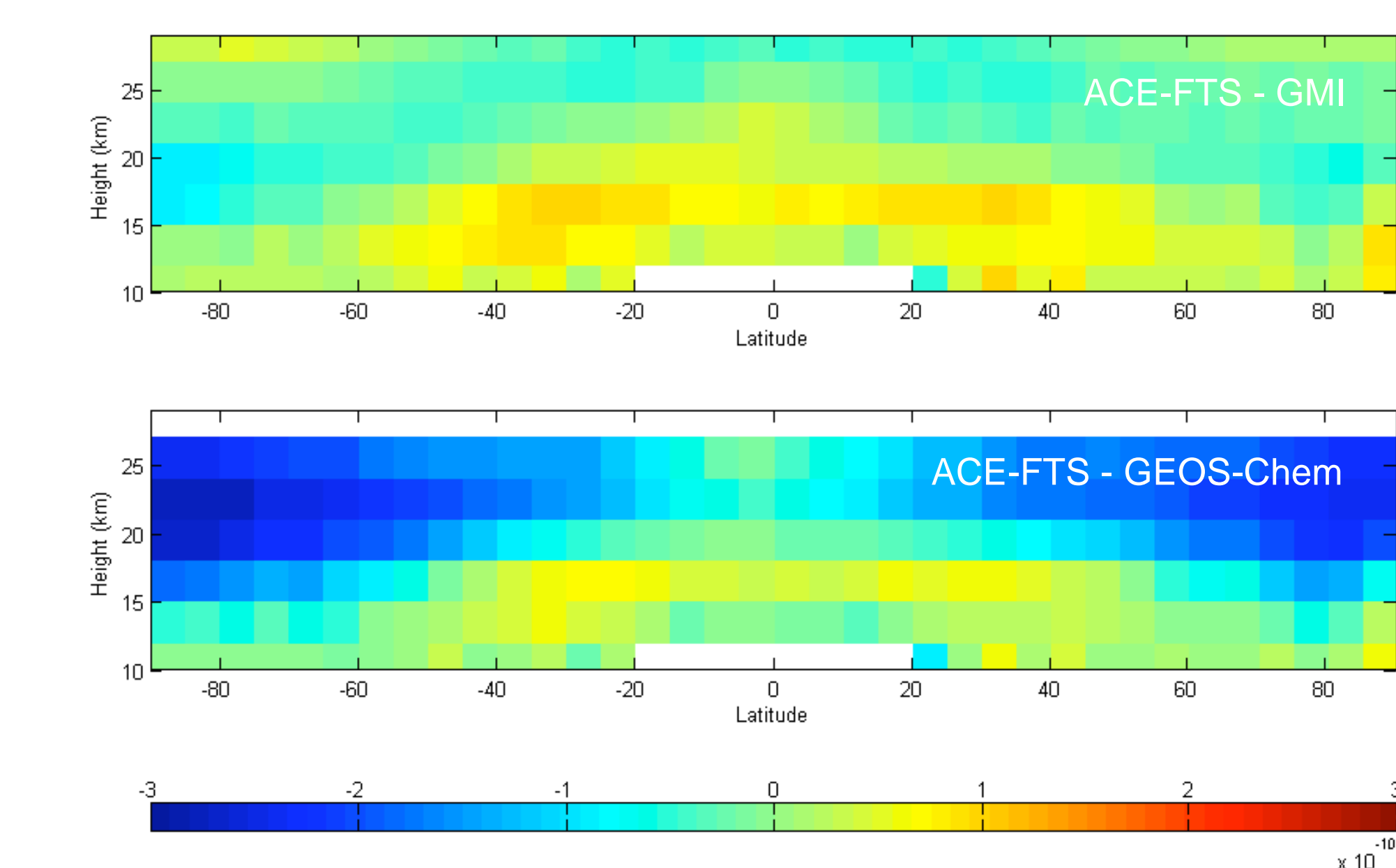
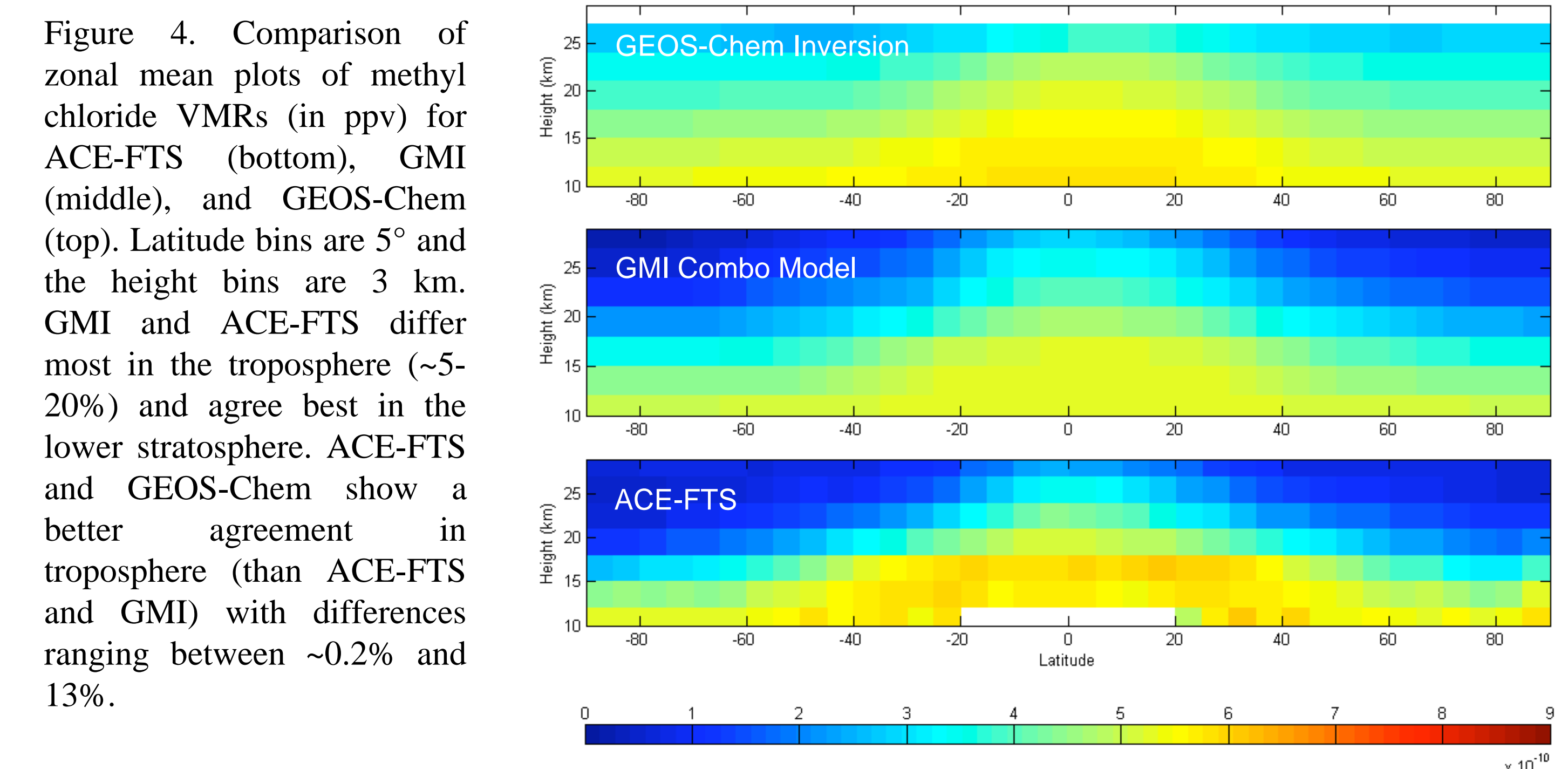


Figure 5. Differences in the zonal mean methyl chloride VMRs (in ppv) for ACE-FTS - GMI (top), and ACE-FTS - GEOS-Chem (bottom). To understand these, differences between the models are being examined, such as the density of levels in the upper troposphere and the lower stratosphere (8 for GEOS-Chem and 13 for GMI; between  $\sim 15$  and 30 km) and methyl chloride sinks in the stratosphere.

**For more information about the ACE mission visit:**  
<http://www.ace.uwaterloo.ca/>

## References

- Bernath, P. F., *et al.*, Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, **32**, L15S01 (2005).  
Bey, I., *et al.*, Global Modeling of Tropospheric Chemistry with Assimilated Meteorology: Model Description and Evaluation, *J. Geophys. Res.*, **106**(D19), 23073-23095 (2001).  
Bloom, S. C., *et al.*, The Goddard Earth Observation System Data Assimilation System, GEOS DAS Version 4.0.3: Documentation and Validation, NASA TM-2005- 104606 V26, 2005.  
Boone, C. D., *et al.*, Retrievals for the Atmospheric Chemistry Experiment Fourier Transform Spectrometer, *Appl. Opt.*, **44**, 7218-7231 (2005).  
Duncan, B. N., *et al.*, Model Study of the Cross-Tropopause Transport of Biomass Burning Pollution, *Atmos. Chem. Phys.*, **7**, 3713-3736 (2007).  
Park, J. H., *et al.*, Spectroscopic Detection of  $\text{CH}_3\text{Cl}$  in the Upper Troposphere and Lower Stratosphere, *Geophys. Res. Lett.*, **13**(8), 765-768 (1986).  
Strahan, S. E., *et al.*, Observationally derived transport diagnostics for the lowermost stratosphere and their application to the GMI chemistry and transport model, *Atmos. Chem. Phys.*, **7**, 2435-2445 (2007).  
Toon, G. C., *et al.*, Comparison of MkIV balloon and ER-2 aircraft measurements of atmospheric trace gases, *J. Geophys. Res.*, **104**(D21), 26779-26790 (1999).  
WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project - Report No. 50, Geneva, 2007.  
Yoshida, Y., *et al.*, Inverse Modelling of the global methyl chloride sources, *J. Geophys. Res.*, **111**, D16307 (2006).  
Zander, R., *et al.*, The 1985 Chlorine and Fluorine Inventories in the Stratosphere Based on ATMOS Observations at  $30^\circ$  North Latitude, *J. Atmos. Chem.*, **15**, 171-186 (1992).  
Zander, R., *et al.*, The 1994 northern midlatitude budget of stratospheric chlorine derived from ATMOS/ATLAS-3 observations, *Geophys. Res. Lett.*, **23**(17), 2357-2360 (1996).

## Acknowledgements

The Atmospheric Chemistry Experiment (ACE), also known as SCISAT-1, is supported primarily by the Canadian Space Agency. This work was funded by the Natural Sciences and Engineering Research Council (NSERC) of Canada. N.W. and C.M. were supported by NSERC through the Undergraduate Student Research Awards program.